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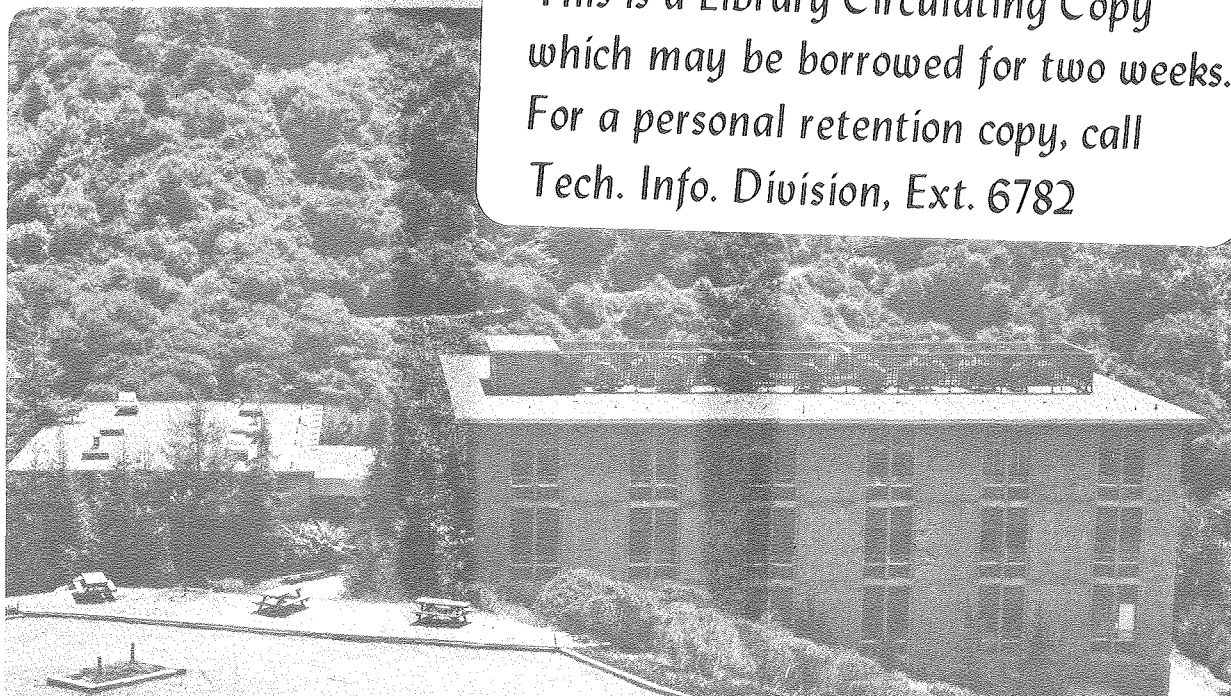
POTASSIUM CATALYZED METHANE PRODUCTION FROM  
GRAPHITE AT LOW TEMPERATURES (473-673 K)

A.L. Cabrera, H. Heinemann, and G.A. Somorjai

April 1981

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LBL-12665  
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POTASSIUM CATALYZED METHANE PRODUCTION FROM  
GRAPHITE AT LOW TEMPERATURES (473-673 K)

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Abstract

The steady state production of methane from high-density pure graphite and water vapor in the temperature range of 473-673 K is reported. The reaction is catalyzed by potassium compounds that are formed on the surface of the graphite. Surface composition is characterized by Auger electron spectroscopy.

This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquifaction Division of the U. S. Department of Energy under Contract W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

## Introduction

Potassium carbonate and potassium hydroxide at present are among the best catalysts used for the gasification of coal with steam to carbon monoxide and hydrogen at high temperatures, in the range of 900-1000 K [1]. In this temperature regime, hydrocarbons are unstable and their formation is not expected [2,3]. There have been no reports of studies of the reaction of water vapor with carbon at lower temperatures where the conditions for the formation of hydrocarbons are more favorable. We have been exploring the possibility of catalyzed conversion of graphite directly to hydrocarbons using various gases as reactants, including H<sub>2</sub>O, H<sub>2</sub>, CO, and CO<sub>2</sub> near 1 atm and at low temperatures (300-700 K), and using potassium as a catalyst. We found no evidence for chemical reactions of the high purity graphite samples with H<sub>2</sub>, CO, or CO<sub>2</sub> in this temperature range. However, in the presence of water vapor, the potassium covered graphite produced methane at a surprisingly low temperature (500 K) and this catalyzed methanation reaction continues for many hours without poisoning.

## Experimental Details

A pyrolytic graphite sample with a surface area of  $\sim 1 \text{ cm}^2$  was mounted on the manipulator of an ultrahigh vacuum system ( $<10^{-9}$  Torr). When the sample holder was positioned properly inside the system, the sample surface was accessible to surface composition analysis by Auger electron spectroscopy (AES), using the cylindrical mirror analyzer (CMA), ion sputter cleaning, and mass spectrometry. The system is also equipped with a high pressure cell which isolates the sample and allows us to perform chemical reaction studies at high pressures (atmospheres). The

product distribution obtained at high pressures were monitored by an HP 5880 A gas chromatograph with a thermal conductivity detector. This system is an improved version of a high pressure-low pressure instrument reported earlier.[4] A schematic diagram of the system with the high pressure cell closed or open is shown in Figure 1. The graphite samples were heated resistively by a high current AC power supply and the sample temperature was monitored by a chromel-alumel thermocouple that was in direct contact with it. Half a monolayer of potassium was then deposited on the graphite using a potassium-zeolite gun at the background pressure of  $1 \times 10^{-9}$  Torr. Then the sample was exposed to a mixture of 30 Torr of vapor obtained from distilled water and 1 atm of helium and heated to the desired temperatures in this gas mixture. It should be noted here that the only sources of hydrogen and oxygen in the system was the water vapor, since the high density graphite sample was free of hydrogen and of oxygen. The cleanliness of the graphite surface and the potassium surface concentration was monitored by AES before and after the high pressure experiments.

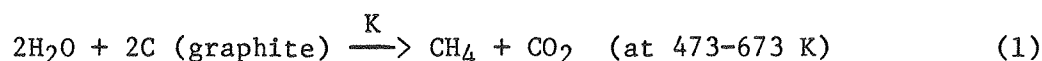
### Results and Discussion

No chemical reaction between graphite and water vapor is detectable in the absence of the potassium catalyst. In the presence of potassium the production of  $\text{CH}_4$  can be readily observed. The concentrations of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{CO}$  produced during the reaction of water vapor and the graphite samples were monitored as a function of time (in the temperature range of 475-600 K). We were also able to detect  $\text{H}_2$  among the reaction products, but due to the similarity of its thermal conductivity to that

of the carrier gas (He), it was difficult to quantitatively follow its concentration change. The buildup of  $\text{CH}_4$  concentration for two temperatures, 475 and 523 K, is displayed in Figure 2. From this figure and similar data obtained at other temperatures, an activation energy for the production of  $\text{CH}_4$  of  $10 \pm 3$  Kcal/mole can be estimated. The turnover frequency for the methane formation reaction is about  $10^{-3} \text{ sec}^{-1}$  at 523 K, assuming that all the graphite surface atoms are active.

The concentrations of  $\text{CO}_2$  and CO that accumulated in the reaction chamber were about 10-30 times higher, respectively, than the  $\text{CH}_4$  concentration. In order to determine whether there were other sources for the formation of the detected reaction products in the high pressure chamber in addition to graphite, several blank experiments were performed. A gold foil with and without potassium was substituted for the high density graphite sample in the chamber and the experiments were repeated using identical conditions of water vapor pressures and temperature. No methane could be detected in this circumstance. However, the production of  $\text{CO}_2$  and CO could be observed at rates that are not too different from those detected in the presence of graphite. It appears that the walls of the stainless steel reaction chamber provide a source of carbon for  $\text{CO}_2$  formation in the presence of water vapor. In order to obtain carbon mass balance for the graphite-water reaction that produces methane, the  $\text{CO}_2$  and CO produced by the blank studies must be subtracted from the total amount of  $\text{CO}_2$  and CO detected under reaction conditions. The buildup of CO and  $\text{CO}_2$  concentrations as a function of time obtained with the gold foil and with the graphite samples for the two temperatures (475 and 513 K) are displayed in Figures 3 and 4, respectively. In the case of CO production, the concentration appears to be independent of temperature

and after subtracting the amount that was produced in the blank experiment, there is no CO left within the experimental sensitivity. However, the CO<sub>2</sub> concentration does depend on temperature and, after subtraction of the amount produced in the blank experiments, some CO<sub>2</sub> still remained, as seen in Figure 4. This amount of CO<sub>2</sub> is comparable to the CH<sub>4</sub> concentration produced at the same temperature. Therefore the reaction that produces CH<sub>4</sub> and CO<sub>2</sub> may be expressed as:



The graphite-water reaction was studied in the temperature range of 473–673 K and it was found that the highest fraction of conversion to CH<sub>4</sub> occurs at 523 K. At temperatures higher than 523 K the potassium surface concentration diminishes and the surface is covered with an increasing concentration of CO as detected by AES; at the same time, the production of CH<sub>4</sub> stops. (CO is present as strongly chemisorbed specie on the sample surface as revealed by thermal desorption experiments.) However, when the CO is removed by argon ion bombardment or by thermal desorption, the production of CH<sub>4</sub> starts up again.

The production of both H<sub>2</sub> and CO<sub>2</sub> was enhanced when CO was added to water vapor. It appears that much of the H<sub>2</sub> and the excess CO<sub>2</sub> are produced by the potassium-catalyzed water-gas shift reaction:



When using mixtures of CO and H<sub>2</sub>O, only H<sub>2</sub> and CO<sub>2</sub> formation could be detected indicating that the water-gas shift reaction was taking place efficiently and at the expense of the methanation reaction. In the

presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  gas mixtures, no products of any kind were detected.

The production of  $\text{CH}_4$  is readily reproducible using a variety of graphite samples and different amounts of potassium. In one of the experiments a sample of graphite was dipped in a KOH solution to rule out the possibility that metallic potassium present on the surface would play a role in the formation of  $\text{CH}_4$ . We obtained in this case the production of  $\text{CH}_4$  in steady state for a period longer than 24 hours.

Potassium appears to catalyze both the reduction of carbon to  $\text{CH}_4$  and its oxidation to  $\text{CO}_2$ . This striking and complex catalytic process will be scrutinized with several surface science techniques in the near future. We shall also explore the possible formation of other hydrocarbons in addition to  $\text{CH}_4$  by the combined use of potassium and transition metal catalysts.

#### References

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Acknowledgement: This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquifaction Division of the U.S. Department of Energy under Contract W-7405-ENG-48 through the Pittsburgh Energy Technology Center, Pittsburgh, Pa.



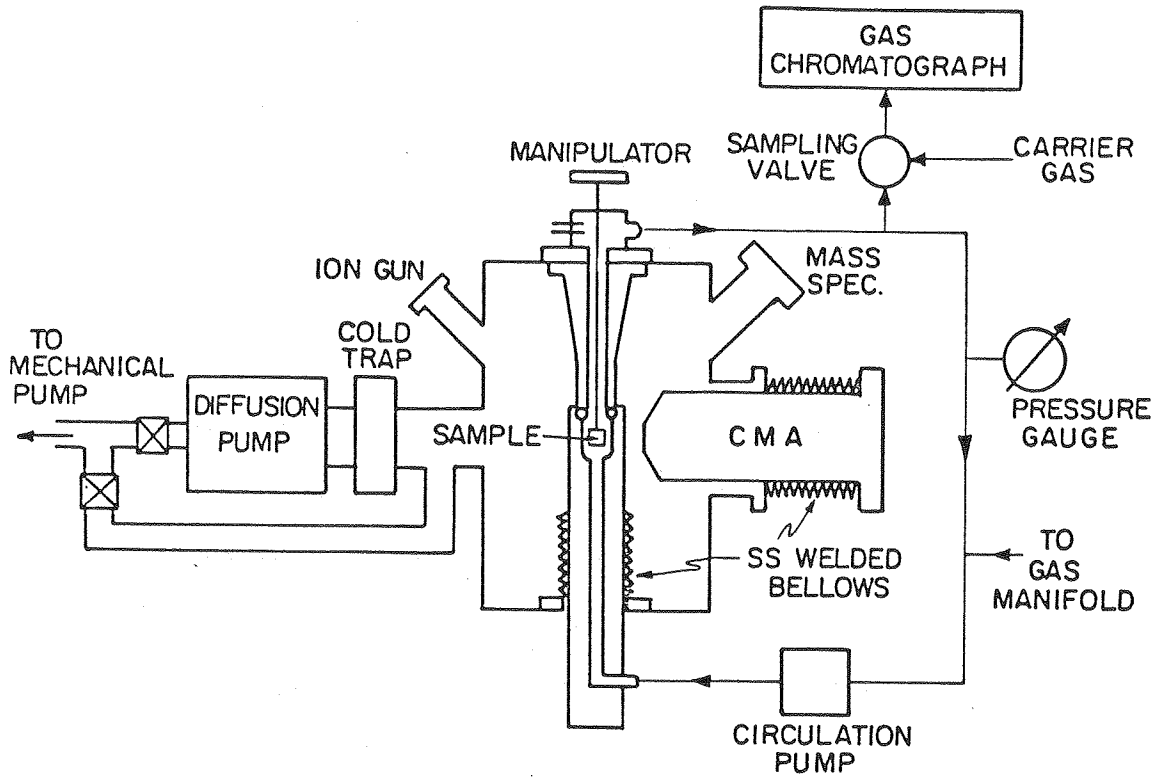
Figure Captions

Figure 1. (a) Schematic diagram of the apparatus with high pressure cell closed, (b) detail with high pressure cell open.

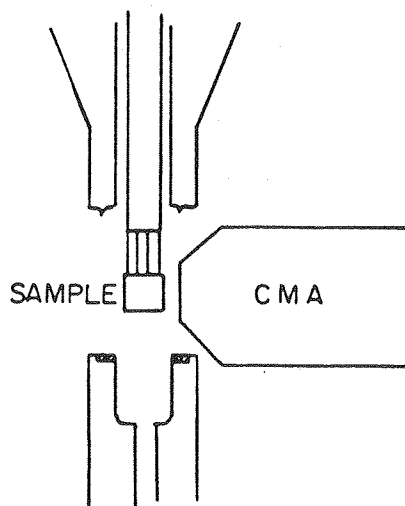
Figure 2. Number of  $\text{CH}_4$  molecules produced during the potassium catalyzed water-graphite reaction as a function of time for two different temperatures.

Figure 3. Number of CO molecules in the gas phase produced as a function of time for two different temperatures. Open circles and triangles correspond to blank experiments performed with potassium covered gold foils. Full circles and triangles correspond to experiments with potassium covered graphite in the reaction chamber.

Figure 4. Number of  $\text{CO}_2$  molecules produced as a function of reaction time for two different temperatures. Dashed curves correspond to blank experiments performed with potassium covered gold foil. Solid lines correspond to experiments with potassium covered graphite in the reaction chamber.



(a)



(b)

Fig. 1

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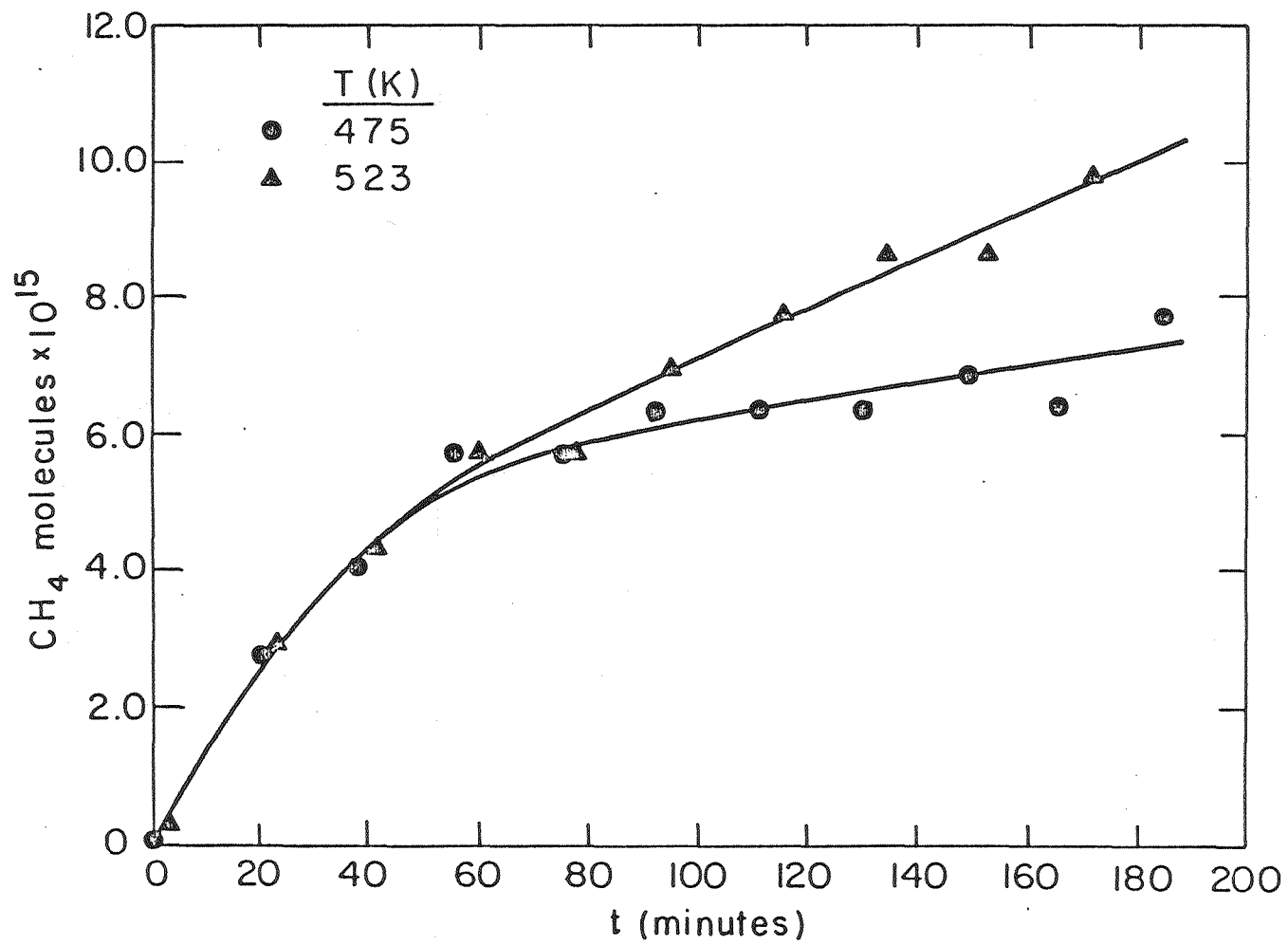


Fig. 2

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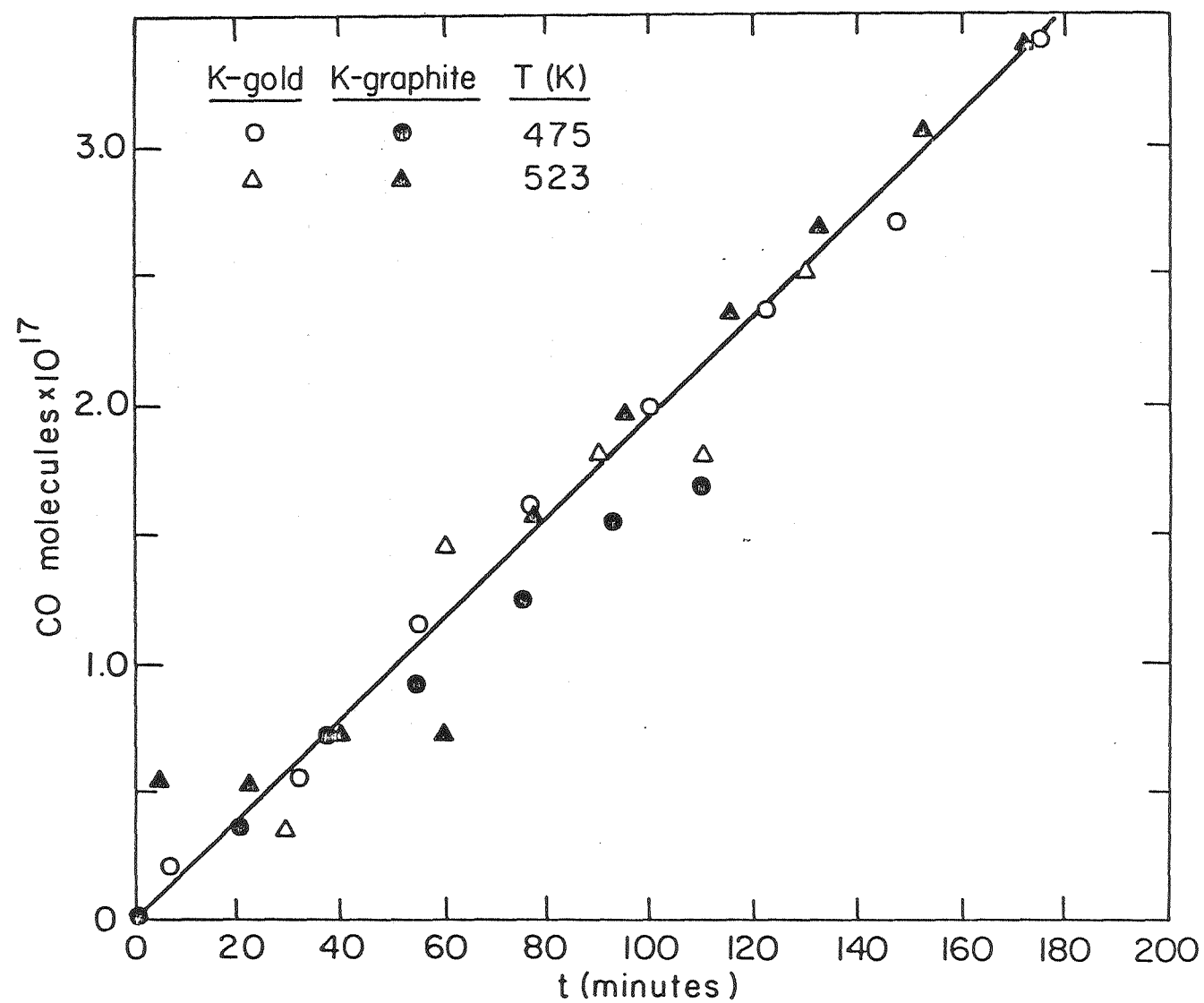


Fig. 3

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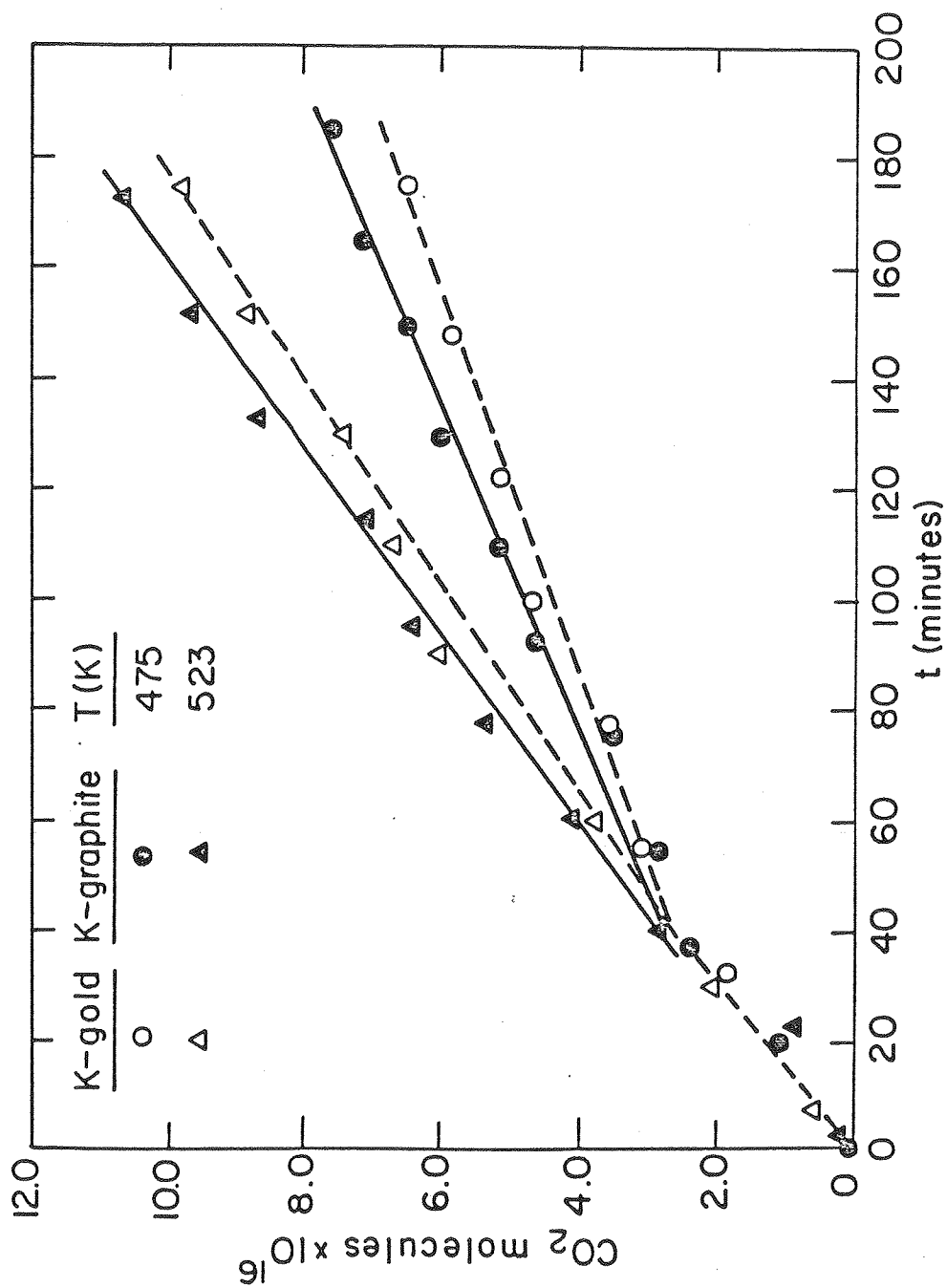


Fig. 4

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